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# LIGHT-EMITTING DIODES WITH VOLTAGE-SWITCHABLE COLORS FROM SEMICONDUCTING POLYMER/POLYMER HETEROJUNCTIONS

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## ABSTRACT

Reversible electroluminescence color changes with applied voltage have been observed in light-emitting diodes fabricated from semiconducting polymer heterojunctions consisting of an electron transporting polybenzobisthiazole and hole transporting poly(*p*-phenylene-vinylene) when layer thicknesses are less than 60–100 nm. Enhanced device performances such as lower turn-on voltage and higher efficiency and luminance were also obtained compared to single-layer devices. The observed voltage-switchable emission colors in these nanoscale heterojunction light sources can be understood in terms of spatial confinement effects which are related to field-dependent charge transport and trapping processes in the materials. These results also demonstrate the use of new high temperature rigid-rod polymers as electron transport and emissive layers in electroluminescent devices.

## INTRODUCTION

Semiconducting polymer/polymer heterojunction structures [1-4] have been used to improve the performances of polymer light-emitting diodes (LEDs) since the first report on conjugated polymer LED [5]. Most of the reported electroluminescent (EL) conjugated polymers are p-type (hole-transport) materials, such as poly(*p*-phenylene vinylenes) (PPV), polythiophenes and poly(phenylenes). Recently, n-type (electron-transport) polymers were reported as the emissive layer or the electron transporting layer in heterojunction LEDs [1-4]. Polymer/polymer heterojunction light-emitting diodes showed balanced electron and hole injection and transport, and hence improved performance of the devices. Yamamoto *et al.* [2] reported the use of an n-type polymer, poly(2,3-diphenylquinoxaline-5,8-diyl), as the emissive layer, and by introducing a p-type hole transporting layer, the electroluminescence efficiency increased about two orders of magnitude. Greenham *et al.* [1] showed the use of a high electron affinity cyano-PPV derivative to form a heterostructure with PPV, resulting in up to 4% EL quantum efficiency. O'Brien *et al.* [4] demonstrated the use of poly(phenyl quinoxaline) as the electron transport layer to give a ten-fold enhanced quantum efficiency compared with the corresponding single layer devices. All these polymer/polymer heterojunction LEDs showed EL emission only from either the n-type layer [1,2] or the p-type layer [4], and no voltage-tunable EL color was observed as reported for polymer blends [6] and organic multilayer devices [7]. Recently we reported [3] finite size effects on electroluminescence of p-type/n-type semiconducting polymer heterojunction LEDs, in which PPV was used as the p-type layer, and a series of polyquinolines were used as the n-type layer. It was found that the PPV/polyquinoline heterojunction light-emitting diodes switch colors reversibly (orange/red  $\leftrightarrow$  green) with applied voltage and showed enhanced performance compared to either single layer devices or bilayer devices with only single-layer emission.

Organic hole-transporting and electron-transporting molecules, such as N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) and 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), respectively, which have been widely used as

charge transport materials in LEDs suffer from their low glass transition temperature or propensity to crystallize. Conjugated rigid-rod polymers, however, have the advantages of high temperature stability, ease of fabrication into large area thin film devices by solution spin-coating, and morphological stability. In this paper, we report semiconducting polymer heterojunction light-emitting diodes with voltage tunable colors using PPV as the p-type layer and polybenzobisthiazoles (PBTPV and PPyBT) as the n-type layer. Poly(benzobisthiazole-1,4-phenylenebisvinylene) (PBTPV) and poly(2,5-pyridylene benzobisthiazole) (PPyBT) are two examples of n-type semiconducting polymers synthesized in our laboratory. Their synthesis, characterization, optical, electrochemical, and charge photogeneration properties have been reported elsewhere [8]. Their n-type characteristics were revealed by electrochemical studies (cyclic voltammetry) [8]. The chemical structures of PPV, PBTPV, and PPyBT are shown in Figure 1.

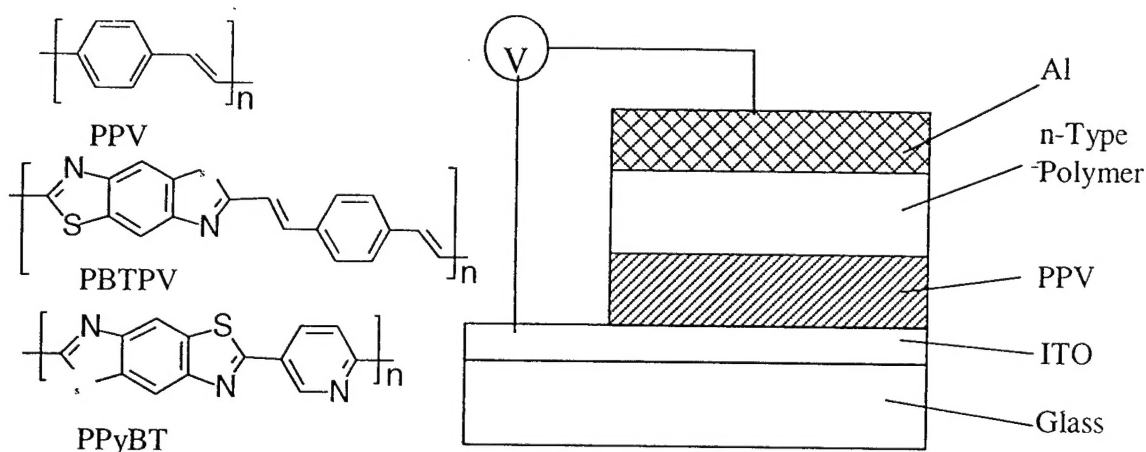


Figure 1. Chemical structures of PPV, PBTPV, and PPyBT, and the schematic of the heterojunction light-emitting diode.

## EXPERIMENTS

The semiconducting polymer heterojunction LEDs were prepared and investigated as sandwich structures between aluminum and indium-tin-oxide (ITO) electrodes as shown in Figure 1. The PPV thin films were deposited onto ITO coated glass by spin coating of the sulfonium precursor from methanol solution followed by thermal conversion in vacuum (250 °C for 1.5 hr). Thin films of PPyBT and PBTPV were spin coated on the PPV layer from their reversibly soluble Lewis acid ( $\text{GaCl}_3$ ) coordination complexes in nitromethane[9]. The film thickness was measured by an Alpha-step profilometer (Tencor Northern) with an accuracy of  $\pm 1$  nm and confirmed by an optical absorption coefficient technique. Finally, 100–130 nm aluminum electrodes were vacuum ( $< 10^{-5}$  torr) evaporated onto the resulting polymer bilayers. Electroluminescence spectra were obtained by using a calibrated Photo Research Model PR-60 photo-colorimeter or using a Spex Fluorolog-2 spectrofluorimeter. Current-voltage-luminance curves were recorded simultaneously by hooking up an HP4155A semiconductor parameter analyzer together with a Grasby S370 optometer equipped with a calibrated luminance sensor head. The EL quantum efficiency of the LEDs was estimated by using procedures similar to that previously reported [10]. All the fabrication and measurements were done under ambient laboratory conditions.

## RESULTS

Figure 2 shows the optical absorption and photoluminescence spectra of PBTPV and PPyBT and the absorption spectrum of PPV. PBTPV has absorption peaks at 475 nm and 508 nm and absorption band edge at 2.1 eV. The emission peak of PBTPV is 630 nm. PPyBT has absorption peaks at 440 and 470 nm and absorption band edge at 2.48 eV. The emission peak of PPyBT is 560 nm. The absorption band edge of PPV is well known to be 2.4 eV [1]. Clearly, there is little overlap between the absorption spectrum of PPV and the emission spectra of PBTPV and PPyBT. Therefore, the emission from the n-type layer will not be absorbed by the p-type layer according to the heterojunction configuration illustrated in Figure 1.

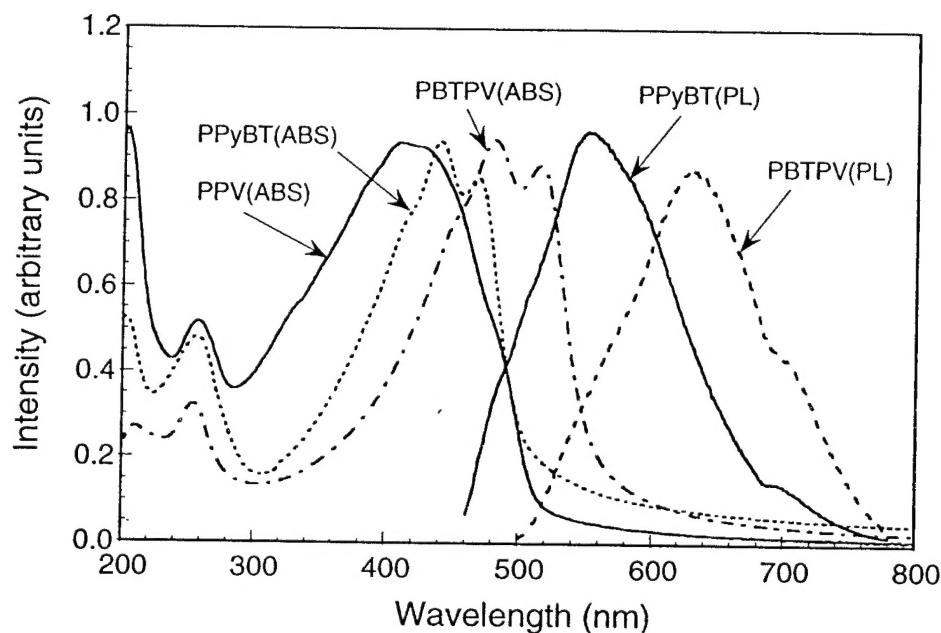


Figure 2. Optical absorption and photoluminescence spectra of PPV, PBTPV and PPyBT.

Figure 3(a) shows representative voltage-switchable electroluminescence spectra for the ITO/PPV(25 nm)/PBTPV(35 nm)/Al device which exhibits a turn-on voltage of 3.5 V. At lower voltages (3.5–17 V), the emission is from the PPV layer, showing its characteristic green EL color; at higher voltages (> 17 V), the emission from the PBTPV layer becomes dominant, showing orange/red EL color. This novel voltage-switchable electroluminescence color is reversible. We also observed that, when the relative thicknesses of the n-type layer and the p-type layer were changed, the emission zone can be within either the p-type layer or the n-type layer. For example, we found that the device ITO/PPV(25nm)/PBTPV(50nm)/Al shows EL emission from only the PBTPV layer at all forward bias voltages as shown in Figure 3(b). Similar results were observed in PPyBT/PPV heterojunction devices. For example, a green EL color was observed in the PPyBT(30 nm)/PPV(25 nm) device; in the PPyBT(65 nm)/PPV(25 nm) device, the EL emission is orange; whereas the PPyBT(40 nm)/PPV(25 nm) device showed strong voltage dependence of EL color going from orange (< 13 V) to green (> 15 V). The observed novel voltage-switchable electroluminescence color

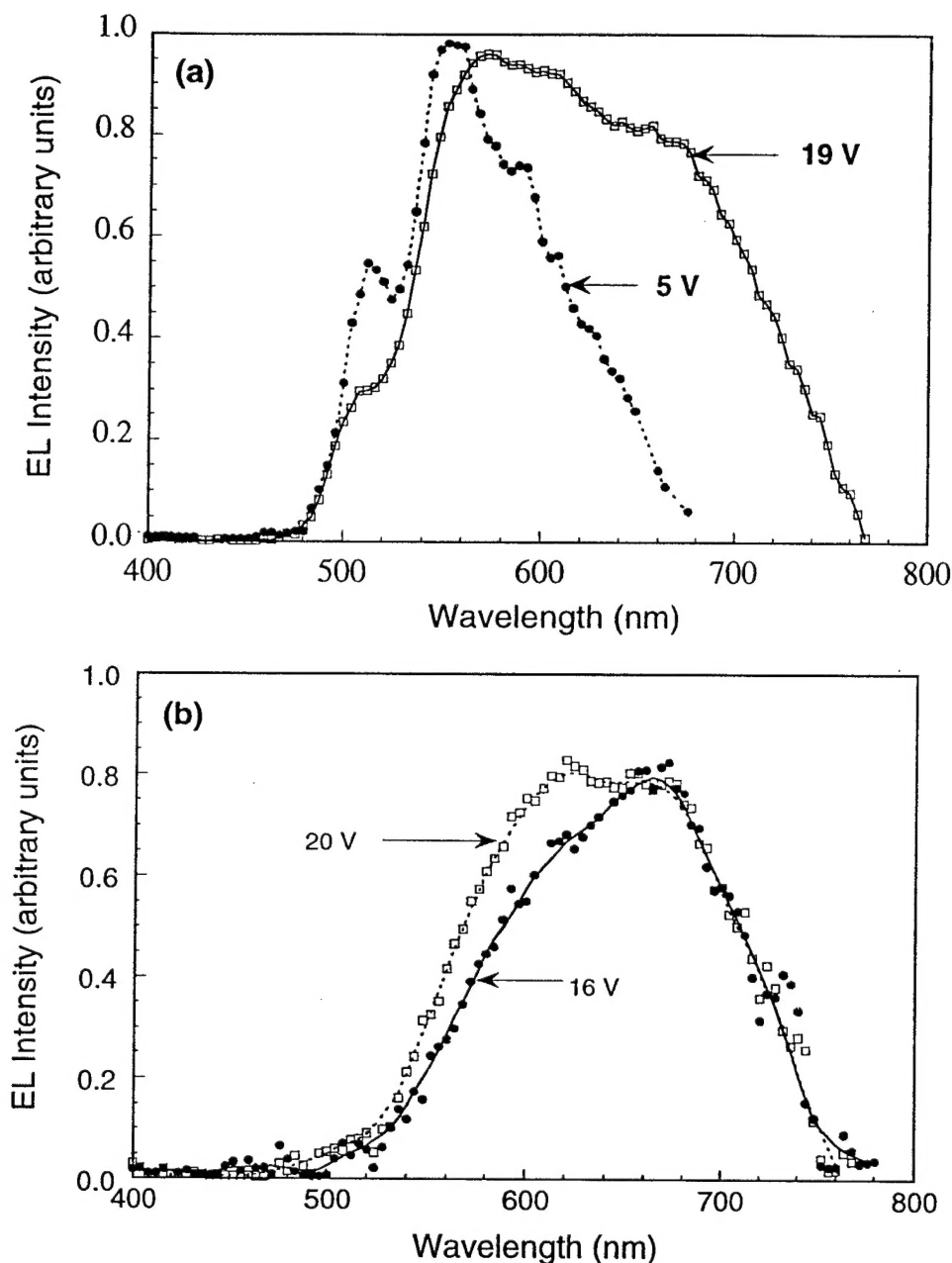


Figure 3. Electroluminescence spectra for: (a) the device ITO/PPV(25 nm)/PBTPV(35 nm)/Al, showing reversible voltage-tunable color emission; (b) the device ITO/PPV(25 nm)/PBTPV(50 nm)/Al, showing the emission only from the PBTPV layer.

is related to the field-dependent charge carriers transport and trapping processes in the polymers as well as the electric-field-dependent bipolar charge transfer characteristic of the polymer/polymer interface [3]. The ranges of charge carriers (electrons and holes) can be expressed as  $x = \mu\tau E$ , where  $x$  is the range of charge carriers,  $\mu$  the mobility,  $\tau$  the lifetime, and  $E$  the electric field. It can be seen that the ranges of charge carriers can be regulated by the electric field through the applied voltage. If the range of electrons is smaller than the thickness of the n-type layer, the polymer/polymer interface is unipolar (only holes can cross

the interface) and the emission from only the n-type layer is obtained. Similar arguments apply to the p-type layer. If the thicknesses of n-type and p-type layers are appropriate, the polymer/polymer interface is unipolar at low field and bipolar (both electrons and holes can cross the interface) at high field and voltage-switchable electroluminescence color can be achieved.

The best results in terms of luminance were obtained by applying a thin layer (15 nm) of PBTPV or PPyBT as the electron transport layer and PPV (60 nm) as the emissive layer. A turn-on voltage of  $\sim 5$  V, luminance of  $\sim 100$   $\text{cd/m}^2$ , and quantum efficiency of  $\sim 0.04\%$  were obtained for the ITO/PPV(60nm)/PPyBT(15nm)/Al device compared to the single layer device ITO/PPV(60 nm)/Al with turn-on voltage of  $\sim 10$  V, luminance of  $\sim 10$   $\text{cd/m}^2$  and quantum efficiency of  $\sim 0.006\%$ . Figure 4 shows the luminance-electric field characteristics of various devices. It can be seen that all the heterojunction devices have lower turn-on voltages than the PPV single layer devices even though the bilayer devices have a larger total thickness. For example, the ITO/PPV(25nm)/PBTPV(35nm)/Al turns on at  $2.4 \times 10^5$  V/cm which corresponds to  $\sim 3.5$  V; the ITO/PPV(60nm)/PPyBT(15nm)/Al turns on at  $\sim 6.7 \times 10^5$  V/cm which corresponds to  $\sim 5$  V; and the single layer device ITO/PPV(60nm)/Al turns on at  $\sim 1.7 \times 10^6$  V/cm which corresponds to  $\sim 10$  V.

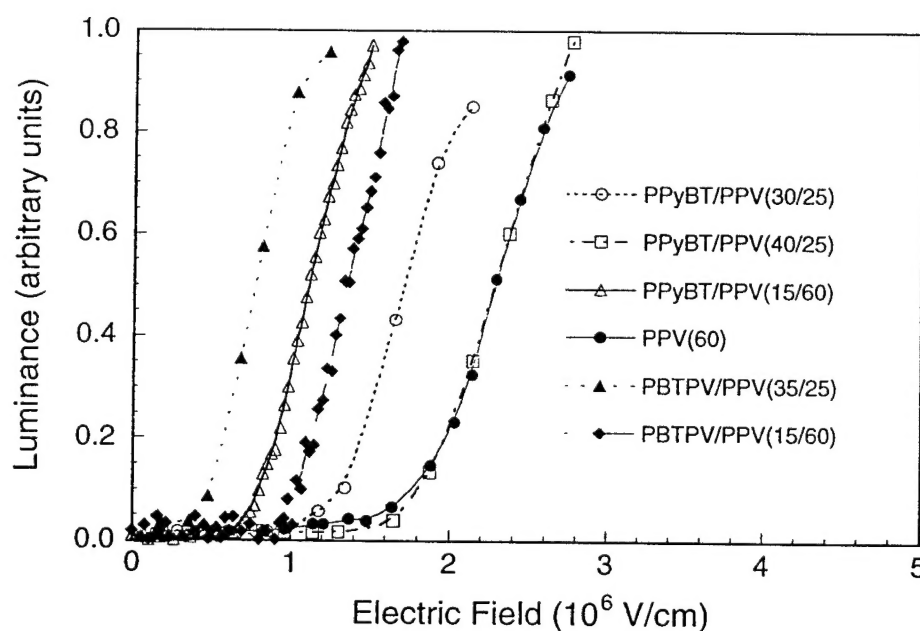


Figure 4. Luminance-electric field characteristics for various devices, the numbers in the parentheses are film thicknesses in nanometers.

Voltage-tunable polymer LEDs have previously been reported for blends of polythiophene derivatives [6]. The voltage-tunable behavior arises from the phase-separated morphology of the blends coupled with radiative and nonradiative energy transfer processes [6]. Such energy transfer processes can prevent EL emission from the higher energy polymer. The morphology of polymer blends strongly depends on the compositions and processing conditions. In polymer/polymer heterojunction devices, we only need to control the thicknesses of the two layers in order to get voltage-switchable EL colors. Because PPV is



insoluble in the solvent of the n-type polymer, the polymer/polymer interfaces in these heterojunctions are well-defined. In polymer/polymer heterojunction LEDs, there is little or no energy transfer because of negligible overlap between the absorption spectrum of PPV and the emission spectra of the n-type polymers and the small interfacial area. Light sources with voltage-tunable colors offered by polymer heterojunctions may have applications in multicolor and full-color displays as well as signaling/control systems analogous to traffic control lighting.

## CONCLUSIONS

We have demonstrated the use of new high temperature, conjugated rigid-rod polymers as electron transport and emissive layers in semiconducting polymer heterojunction LEDs. It was found that reversible voltage-switchable LED colors can be achieved from n-type/p-type polymer heterojunctions by controlling the thicknesses of both layers. Furthermore, the EL emission can be from either the n-type or the p-type layer depending on the thicknesses of those layers. The observed voltage-switchable EL colors in these nanoscale heterojunction LEDs are related to the field-dependent charge transport and trapping processes in semiconducting polymers and result from the small and field-dependent ranges of charge carriers. The performances of the heterojunction LEDs were greatly improved compared to single-layer devices. One order of magnitude enhancement in luminance and a turn-on voltage as low as 3.5 V were observed in heterojunction devices compared to PPV single-layer devices.

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